Supporting Information for

"The Role of PufX in Photochemical Charge Separation in the RC-LH1 Complex from *Rhodobacter Sphaeroides*: An Ultrafast MidIR Pump-Probe Investigation"

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NearIR pump probe measurements on RC-LHI-X- complexes.

Energy transfer and charge separation were also investigated in the near-infrared between between 750 and 950 nm, with excitation at 800 nm. Experimental information on ultrafast spectroscopy and data analysis can be found in the main text. Figure S1 shows EADS obtained from a global analysis of data recorded for RC-LHI-X- complexes in the presence of ascorbate and PMS. Five components were required to model the data, with lifetimes of 0.1, 1.5, 43, 292 ps and an infinite component. The first component, with a lifetime of 110fs, might still be affected by the coherent artifact, given that its lifetime is similar to the instrument response function (~120 fs). Hence, it is not discussed any further.

The remaining EADS were dominated by the broad LH1 contribution around 885 nm. The contribution of the RC, with marker bands at 760, 800 and 867 nm was entirely overshadowed by those of the antenna. Hence, precise statements about energy transfer between the antenna and the reaction center are difficult to make. The lifetimes of the EADS were in reasonable agreement with those obtained from the mid-IR spectroscopy (see Figure 4, main text)

The loss of about 20 % in amplitude in the 1.5 ps component around 885 nm was most likely due to exciton-exciton annihilation in the antenna ring [1], rather than transfer to the RC, which takes 20-70 ps [2-6]. Both the loss in amplitude and the lifetime are in good agreement with what was found in the mid-IR.

The relative large size of the LH1 signals compared to those of the RC and the amplitude of the final spectrum, has been observed before for this kind of system and can be explained by excitonic interactions of the BChls arranged in a packed circular symmetric structure [7-9]. In brief, due to the collective nature of the initial excitation, absorption of one photon by the antenna can lead to an absorbance difference signal with a magnitude which corresponds to the bleaching of several monomeric BChl molecules [10].

The 43 ps and 293 ps spectra were very similar in the antenna region, apart from another 20% loss in amplitude. In the RC region between 750-850 nm, the 800 nm bandshift signal typical for P^+ formation [11]) can be identified, and the EADS of the final component for RC-LH1-X- complexes resembled that of isolated RCs quite well (Fig. S2). However, it is clear that in the midIR the spectral features associated with LH1 and the RC are more balanced in amplitude, richer in detail and provide therefore a more valuable tool for following the electron transfer process in the RC in the presence of LH1.

Reproducibility and averaging.

Reproducibility of the experimental findings is illustrated in Figure S3. The EADS shown in black are from the dataset described in detail in the main text, whereas the EADS in red are from a duplicate experiment under identical conditions. Reproducibility in the pattern of positive and negative bands in the fingerprint region between 1680 and 1640 cm^{-1} was good between the two experiments carried out on a particular type of sample. A calculated average of the two EADS for each type of sample is shown in green.

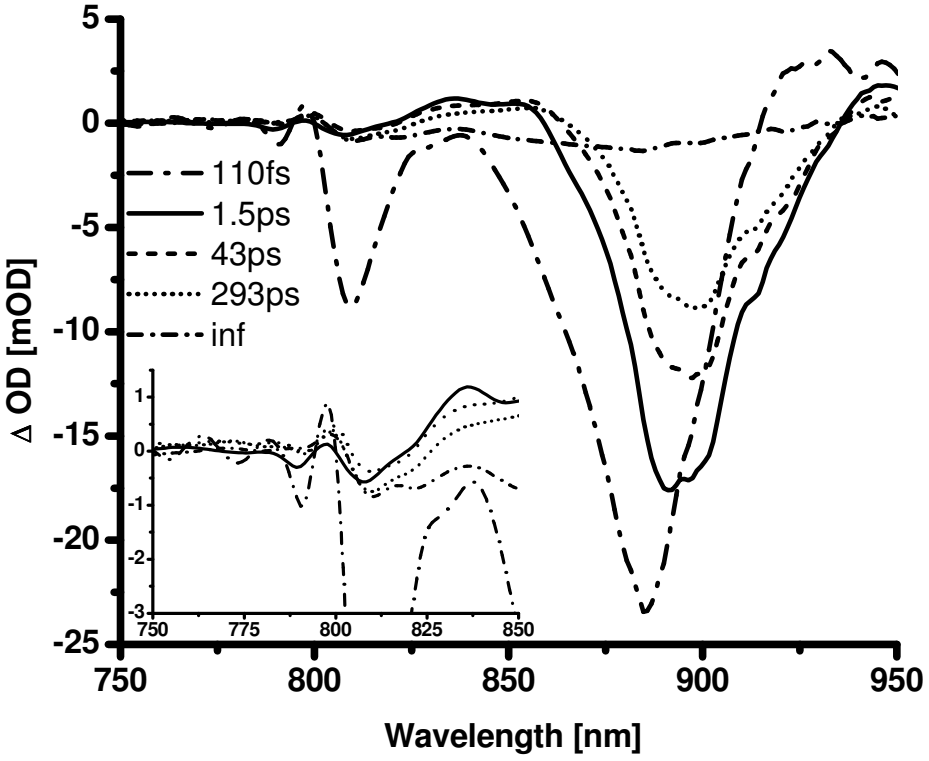

Figure S1. EADS obtained for RC-LHI-X- complexes after 800 nm excitation, with detection in the near-infrared.

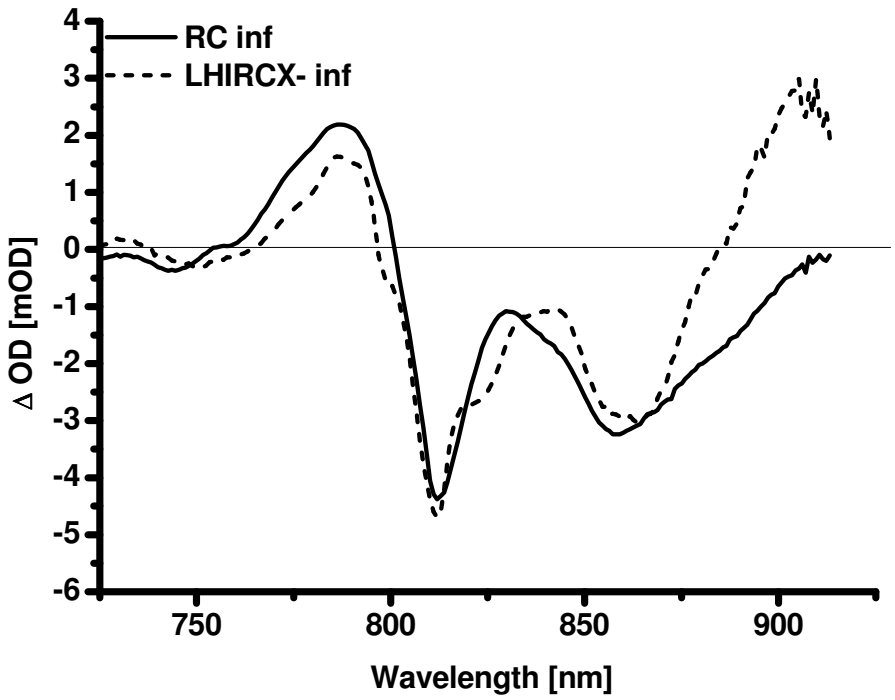

Figure S2: EADS of the final component for the RC and RC-LH1-X- complex.

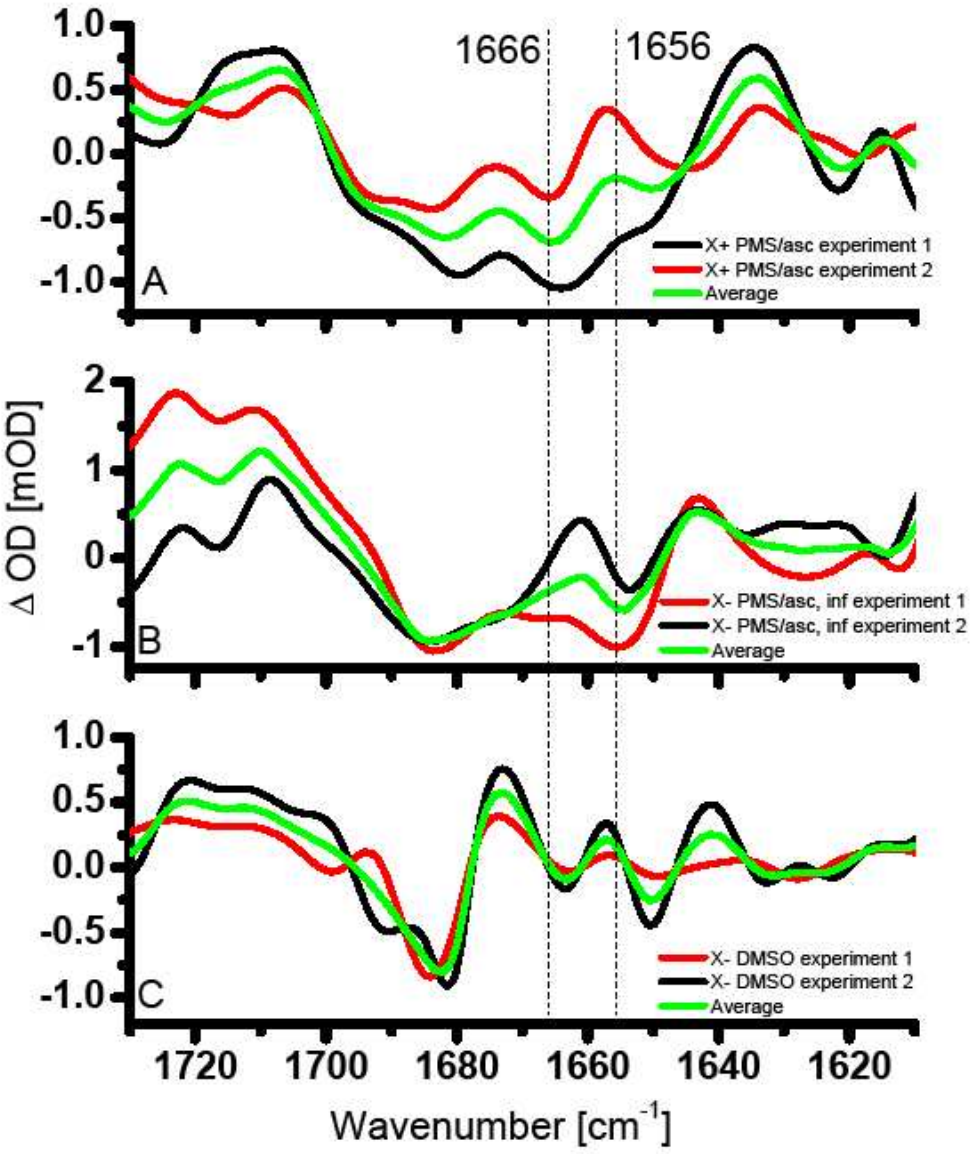

Figure S3. Reproducibility of final EADS for RC-LH1 complexes under reducing and oxidizing conditions. . Key: black – experiment 1, as described in main text; red – duplicate experiment under identical conditions; green – average of black and red spectrum,

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